

Comets: Role and Importance to Exobiology

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Comets have been repeatedly linked with exobiology for the following reasons:

1. Among the heavenly bodies, they contain the largest amount of organic molecules;
2. The observed comets are all in unstable orbits; since they cross the planetary orbits, orbital precession guarantees that sooner or later comets hit the planets. Hence they are a possible source of water, carbon, and organic molecules for the planets;
3. Comets decay into gas and dust; this is a source of interplanetary particles that may also reach the planets. As expected, interplanetary particles collected high in the atmosphere of the Earth also contain organic molecules;

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4. Comets show a strong analogy with carbonaceous chondrites; as a matter of fact, if a large carbonaceous chondrite were on a cometary orbit, it would be indistinguishable from a comet. In particular, it would develop a cometary tail, and the spectrum of its head would also be indistinguishable from a cometary spectrum;

5. The previous analogy has been extended to Mg 26 (extinct Al 26) observed in many chondrules. If also present in comets, Al 26 would have produced a transient source of heat (it decays with a half-life of 0.7 million years) large enough to keep water in the liquid state in the cores of comets for a time long enough to make complex organic syntheses from prebiotic molecules possible;

6. Fossil evidence confirms a chain of events suggesting that comets are the major source of the oceans and of the atmosphere of the Earth, as well as that of the organic compounds that were needed to get life started on the Earth;

7. The previous chain of events can be traced backward to interstellar space, namely to those dense interstellar clouds that contain numerous organic molecules produced by ion-molecular reactions. Comets seem therefore to be the cosmic messengers that have transported organic molecules from the interstellar space down to Earth, mostly during the late stages of the accretion of the terrestrial planets.

The understanding of the chemical nature of the cometary nucleus has considerably progressed recently, in particular thanks to the multiple flybys of comet Halley. Most of the questions of exobiological interest have therefore received much attention, but none have been unequivocally answered. The basic reason is that the relevant molecules were damaged by the high velocity of the flyby prior to analysis. What we know now about cometary chemistry is reviewed in the following section.

In the last decade, considerable progress has also been achieved in the understanding of the chain of events whose outcome was the biosphere of the Earth. Crater statistics on the Moon have not only numerically con-

firmed the early intensity of the cometary bombardment of the Earth, but numerous other fossil data from meteorites (mentioned later) are consistent with the sequence of earlier events that explain the mechanism of this bombardment. It will be shown in particular how the general scenario describing the origin of the solar system also explains the exogenous origin of the terrestrial planets' atmospheres.

Since organic molecules are ubiquitous in the Cosmos, cometary processes that bring organic molecules from space to rocky planets seem to be an integral part of the chain of events forming planetary systems, a conclusion of far-reaching importance for exobiology.

Chemistry of the Cometary Nucleus

Radial Homogeneity of Nucleus

Quantitative knowledge about cometary chemistry has mostly been derived from the bright comets of the 1970s and complemented by the wealth of information brought about by the flybys of comet Halley during its 1986 passage. However, other historical comets have displayed enough diversity to suggest the existence of large physical and chemical differences.

The author reviewed this matter in 1987 and has come to the conclusion that in spite of their apparent diversity, comets represent a population of essentially homogeneous objects. In 1982, he also listed circumstantial arguments that all favor undifferentiated nuclei. The gist of the arguments is that, if nuclei were radially differentiated, their decay with aging or their fragmentation by splitting would sooner or later produce observable changes. However, all observations of cometary material that originated at different depths in the pris-

tine nucleus show the same properties, namely:

1. The same dust-to-gas distribution pattern;
2. The same spectral composition of the volatiles;
3. The same structural strength against fragmentation;
4. The same vaporization pattern after fragmentation.

Of course, minor heterogeneities would not be observable below a certain size (30 to 50 meters). There are, however, surface differentiation effects. They probably preexist in "new" comets, because of their surface irradiation by galactic cosmic rays. Of course, as soon as a comet penetrates the inner solar system, the outgassing of the surface layers and the sintering of dust into a crustal slag enhances the surface differentiation considerably.

The apparent diversity of the cometary population comes more from the nucleus fragmentation and decay, than from any physical or chemical difference in the pristine component.

The Dust-to-Ice Ratio

By definition, a "primitive" mixture is the condensate at 30 K of a gas of solar composition. At such a low temperature, hydrogen, helium, and neon (that is, the most volatile gases) do not condense. Therefore, they are considerably depleted in a primitive mixture, whereas all the other elements have remained in solar proportions; in particular, carbon, nitrogen, oxygen, and sulfur are not depleted. It is worth mentioning that the most primitive carbonaceous chondrites do not come straight from a primitive mixture, since their carbon, nitrogen, oxygen, and sulfur are depleted in variable amounts. In a primitive mixture, all metals including silicon, iron and magnesium are assumed to be more or less oxidized into silicates. The amount of oxygen used for that purpose depends somewhat on the nature of the silicates: the fraction oxygen/metals may go from a low 4/3 for olivine (in numbers of

atoms) to a high 9/5 for serpentine. Assuming that the rest of the oxygen as well as C, N, and S is in the volatile ices, then the primitive dust-to-ice mass ratio goes from 0.54 to 0.66 if Cameron's (1973) abundance table is used; it goes from 0.61 to 0.76 if we use strictly solar data. Including possible uncertainties, the primitive ratio remains in the range of 0.65 ± 0.11 , if *all* the carbon is in volatile compounds (like CH_4 , CO , or CO_2). If 3/4 of the carbon is in refractory compounds, as was observed in the dust grains of comet Halley, then the "primitive" ratio becomes 1.10 ± 0.22 . To summarize the situation, depending on where most organic molecules go (in the refractory dust or in the volatile ices), the primitive dust-to-ice ratio may vary from 0.5 to 1.3.

The notion of primitive ratio is useful because it sets a lower limit for the dust-to-ice mass ratio. If comets condensed or accreted at a very low temperature from a reservoir of solar abundances and were never processed by heat later on, then the dust-to-ice ratio is the primitive ratio. If comets were heated during the course of their evolution, they lost more gas than dust; some of the gas may also get polymerized into dust; hence, the dust-to-ice ratio becomes larger than the primitive ratio. This is likely

to occur locally, in the outer layers of the nucleus, first after their irradiation with cosmic rays, second in the crustal slag after perihelion passage. It is difficult to conceive any phenomenon that could diminish the primitive ratio by losing more refractory material than volatile stuff.

The actual dust-to-ice ratio of pristine comets is difficult to establish, because the surface decay of the nucleus alters the ratio. However, the interpretation of large outbursts suggests that the sudden blow-off of a mantle of dust often occurs. Ratio fluctuations out of steady state have been reconstructed day after day from data obtained during the outburst of comet Arend-Roland. After the outburst, the dust-to-gas mass ratio seemed to go back asymptotically to its steady-state value; for this reason it is believed that the steady state is representative of the inner composition of the nucleus. The best values for the steady-state dust-to-gas ratio have probably been obtained by the Finson-Probst method for two comets only. They are 0.8 ± 0.2 and 0.6 ± 0.4 for comets Arend-Roland and Bennett, respectively. Because of the error bars, the results are not essentially different and are consistent with a primitive ratio in each case.

The Vega experiments have found 5 to 10 tons/second of dust and 30 tons of gas for the production rate of comet Halley, but a study of the tail isophotes has shown that the dust-to-gas ratio during the flybys was far from the steady state. At any rate, the discrete data of the Dust Impact Detection System (DIDSY) carried by the Giotto Spacecraft suggest the existence of a large population of massive particles not taken into account in the production rate of dust found by the Vega experiment. Comet Halley's dust-to-ice ratio remains therefore remarkably consistent with a primitive ratio.

The dust-to-gas mass ratio in the coma of 17 comets has been studied, and very low values, between 0.05 and 0.30, were found. Of course a comet, even with a primitive ratio, may vaporize more gas than dust when not at a steady state, but this cannot last for a long time without choking the vaporization under a growing mantle of outgassed dust. On the other hand, it is unlikely that the 17 comets all showed lower values than the steady state. Assumptions were made: an albedo of 0.05 for dust and a nominal expansion rate of

Table 10-1: Dust in Comet Halley.
Mean Chemical Composition in Mass %

Organic 33%		Inorganic 67%	
Unsat. hydroc.	16.0%	Silicates	51.5%
H, C + O	5.2%	FeS (troilite)	6.0%
H, C + N	4.5%	C (graphite)	3.0%
H, C + S	1.8%	S (sulfur)	1.0%
Water	5.5%	Water	5.0%

1 km/second for gas. Additionally, an assumption was made on the grain size distribution of the dust that was not measured, since the Finson-Probst method was not used on the dust tail isophotes. Since the existence of a steady state was not established for any of the cases, no hard inconsistency has been found with a primitive dust-to-ice ratio of 0.5 to 1.3 for the 17 comets in question.

Nature of the Dust Grains

Before the flybys of comet Halley, Brownlee particles collected by NASA's U2 plane in the upper atmosphere were probably the most reliable source of information on the cometary grains. Their analysis suggested that they were similar to carbonaceous chondrites, containing, however, more carbon and sulfur. Typically, the particles contained 5% C by mass,

instead of 2.5 and 3.2%, the median, respectively, for CM and CV chondrites.

Yet the balance sheet for carbon in comets suggested that 3/4 of the cosmic carbon was still missing. At that time, I proposed that cometary dust could contain up to 30% carbon by mass, in order to reach cosmic abundances. The dust results of the Vega 1 flyby of comet Halley have supported this view rather well, although they revealed that the individual dust grains vary greatly in mass and in composition. A chondritic silicate fraction without carbon seems to form the grain core, which is embedded in a variable amount of organic material. Most of the grains are from 0.2 to 1.0 μm in diameter, with a steep decrease in the number of larger-sized grains. Table 10-1 represents the mean composition averaged over 80 particles.

The bulk of the carbon is, of course, in the organic fraction; an extra amount of 3% reduced carbon, presumably graphite, is also counted with the inorganic fraction. With this amount of carbon in the dust, the problem of the apparent carbon deficiency in comets seems to have completely vanished.

The inorganic fraction (67% in mass) contains 51.5% silicates (mainly of magnesium and iron), 6% troilite FeS, 3% carbon, 1% sulfur, and 5.5% water.

The organic fraction contains 16% hydrocarbons with an H/C ratio close to 2/3, suggesting unsaturated hydrocarbons like C_3H_2 ; there are also 5.2% of oxygen-containing species, probably formic acid and formaldehyde in about equal amounts, and 4.5% nitrogen-containing species, a mixture of hydrogen cyanide, acetonitrile, aminoethylene, pyrrole, pyridine, pyrimidine (50 coincidence pairs in mass spectra); purines and adenine would also be present in several grains, whereas there is no indication for amino acids; finally, there is 1.8% of sulfur-containing species. Some molecules contain several oligo elements; amino methanol seems to be present, as well as some O's that seem

to be occasionally exchanged by an S atom in several organic molecules.

If recently published identifications are all correct, they imply very important conclusions for exobiology, namely:

1. The prebiotic molecules HCN, H₂CO, and H₂O are present;
2. The precursors of the nucleic bases (purines and pyrimidines) are probably present;
3. The amino acids are apparently absent.

However, insufficient details are available to check the validity of the method used. The contentious nature of the results (in particular items 2 and 3 above) stems from the 78 km/second velocity of the flyby. The high-velocity impact of the dust grains on the neutral mass spectrometer not only vaporizes grains but destroys molecules into atomic and molecular fragments. It is surprising that during impact large condensed heterocycles retain a recognizable spectral pattern of molecular fragments, but this has been verified in the laboratory for velocities up to 10 km/second. At any rate, the matter is pending if only because of the dramatic significance of the possible results.

Thanks to the large amount of organic material in the dust of comet Halley, there is no doubt now that the abundance of all elements, including the light elements C, N, O, and S, are present in almost cosmic proportions in this comet, with the exception of H (and presumably undetected He and Ne), depleted by a factor of about 500. The same situation is likely to exist in other comets.

Another important conclusion is the presence of a large fraction of rather volatile molecules in the CHON particles: 15 to 30% of the so-called "dust" is probably formed with "icy" molecules that may be almost as volatile as, and even possibly more volatile than, water; therefore they must vaporize according to the "icy grain halo" model. In particular, their decay may explain the existence of an extended source of some of the gaseous species observed around the nucleus, and extending into the coma.

For example, formaldehyde has been observed in the CHON particles (those particles that contain only C, H, O, and N atoms); its mass seems to represent several percent in mass of the total dust. Formaldehyde is more volatile than water; it has also been identified in the gaseous coma; its photodissociation by the solar light takes place in a few 10³ seconds; and its branching ratio into CO plus other fragments (H₂ or H + H) is 69%. However, it can be freed by grains with a lifetime of a few 10⁴ seconds and it can explain the observed extended source of CO.

Table 10-2: Light Elements in Some Bright Comets.
Mean Abundances in Volatile Fraction

Element	Bright comets	Comet Halley
H	1.8 ± 0.4	1.9 ± 0.4
C	0.20 ± 0.10	0.20 ± 0.05
N	0.10 ± 0.05	0.10 ± 0.05
O	1.00	1.00
S	0.003 ± 0.002	0.01 ± 0.005

All elements are normalized to oxygen = 1.0.

Origin of the Dust in Comets

Some cometary grains contain metals or silicates only; some other grains contain a silicate core plus a variable mantle of organic molecules. Finally, the CHON grains do not contain metals at all, only organic molecules. The grains—most in the 0.2 to 1.0 μm range—are sufficiently different chemically to imply that they were condensed at different places and brought together (before or during accretion) by a process comparable by all means to sedimentation. This is rather similar to the carbonaceous chondrites which also contain a mixture of fine grains of different origins, namely high-temperature and low-temperature grains, oxidized and reduced grains, hydrated and anhydrous grains, etc.

The most plausible place for this sedimentation to happen has been described in models of the solar nebula. When the turbulence subsides because mass transfer to the accretion disk has stopped, then dust separates from the gas and sediments into equatorial rings, thereby preparing the stage for the accretion of planetesimals. In this scenario, the dust of carbonaceous chondrites has sedimented in the outer asteroid ring and the frosty and icy cometary dust has sedimented at distances between those of Jupiter and Neptune or beyond.

The recent observations of the chemical diversity of the dust in comet Halley seems to be consistent with such a scenario. Recent proposals that reconsider alternate origins for comets may have difficulties in explaining the chemical diversity of their dust grains.

Nature of the Volatile Fraction

There is a deep similarity in the spectra of many comets in the visual and the beginning of the ultraviolet. Many early differences came from observational artifacts (spectral and spatial dispersion, sensitivity limits of the photographic plate, etc.). The same remark has been expressed for the vacuum ultraviolet, suggesting that there might be a deep similarity in the composition of most comets.

It has been established that comets Bennett 1970 II, Kohoutek 1973 XII, and West 1976 VI were similar in many respects. After careful discussion, the elemental ratios of H, C, N, O, and S in their volatile fraction were found to be close enough to be incorporated into a single model, representing “the average bright comet of the 1970s.” The final model is given in table 10-2.

It is worth mentioning that the elemental ratios of comet Kohoutek were oscillating wildly; the observations had picked up epochs close to two outbursts and far from steady state. It was, however, possible to make use of the observations. An outburst propagates in a few days into the coma; because of their longer photodecay lifetimes, the H atoms had been produced an average of 11 days earlier than the OH radicals observed simultaneously. Correcting for the delays damped the spurious fluctuations due to the outbursts and yielded a ratio $H/OH = 1.8 \pm 0.8$ for the same production epoch of H and OH. In the same way, when C and O were corrected for the two different ionization lags of 2 days and 5 days respectively, the C/O ratio yielded an average of 0.22 ± 0.06 for Kohoutek (close to 0.21 ± 0.03 for the comet West), making the two spurious ratios of 0.08 (January 5) and 0.58 (January 8) disappear. This example has been discussed in detail to show that early differences came more from deficiencies in the models than from actual compositional differences.

The complete quantitative molecular analysis of the volatile fraction remains, however, a difficult feat, because the number of species involved remains uncertain, and the excitation mechanisms that bring different molecules into visibility in the spectra remain intricate. As far as the traditional bands observed in the visual are concerned, spectral differences from comet to comet are small and concentrate around the same "normal" ratios, for instance, $C_3/CN = 0.2$ and $C_2/CN = 1.5$.

The situation is somewhat different in the vacuum ultraviolet, where major carbon compounds seem to be variable in some comets. The diversity of the CO/OH ratio in comets Kohoutek 1973 XII, West 1976 VI, and Bradfield 1979 X has been mentioned in others' work. The interpretation of the two outbursts of comet Kohoutek given in the previous paragraph is convincing enough not to attach any significance to the spurious value 0.58, but the very low value of $CO/OH = 0.044$ of comet Bradfield has not been explained. It could come either from the same type of fluctuation out of steady state, or from genuine elemental differences.

It has been suggested that the variability of the CO/H₂ ratio is large: 27% for West, 18% for Halley, and 1% for Bradfield. The differences do not necessarily reflect intrinsic compositional differences between comets, but may come from deficiencies in the models used to interpret the observations.

The CO Distribution in Comet Halley

Many observations have been collected on or near the dates of the comet Halley flybys. For this reason, the CO distribution in comet Halley needs a separate discussion. Not surprisingly, important discoveries come from the flybys themselves.

The Giotto neutral gas mass spectrometer has discovered the existence in the coma of a large source of CO extending up to 15,000 km from the cometary nucleus. Independently, a large organic fraction containing, in particular, formaldehyde (H_2CO) and formic acid (HCO-OH) was discovered in the dust grains analyzed by the dust impact gas spectrometer PUMA of the Vega 1 spacecraft. Although the two groups have not yet mentioned the correlation between these two discoveries, we will verify in the next section that the photodissociation of H_2CO and of HCO-OH from the volatile fraction of the grains explains quantitatively the origin of the extended source of CO. Other explanations do not seem therefore to be justified.

From Giotto data reported in 1986, the punctual CO source represents 40% and the extended source 60% of the total CO flux. A total production of $\text{CO}/\text{H}_2\text{O} = (10 \pm 5)\%$ is given. The error bar is wide because other molecular fragments might contribute to the 28 a.m.u. peak. Since N_2 is the other major contributor to the peak, we have used the feedback of the very low evaluation of the total elemental N coming from other data (table 10-2), to deduce that the actual value of $\text{CO}/\text{H}_2\text{O}$ lies in the upper range of limits, and can be reasonably represented by $\text{CO}/\text{H}_2\text{O} = (13 \pm 3)\%$.

The other source of information on CO comes from the vacuum ultraviolet spectra, from which $\text{CO}/\text{OH} = (10 \pm 5)\%$ was reported; however, because of the discovery of formic acid whose photodissociation represents another source of OH, we must remain aware that more than ever OH is not an automatic measure of H_2O . The $\text{CO} = 10\%$ reported from the Pioneer Venus spacecraft should not be construed as an identical result to the vacuum ultraviolet spectra results. The carbon resonance line used for the previous ratio represents only somewhat more than one-half of the total carbon, because the rest has

remained in ionized CO^+ blown away at a high velocity by the solar wind.

Finally, other researchers give $\text{CO}/\text{H}_2\text{O} = (20 \pm 5)\%$ on February 26, 1986, and $(17 \pm 4)\%$ on March 13. Only the latter is close enough to the Giotto flyby to be compared and used here. We conclude this discussion by adopting

$$\text{CO}/\text{H}_2\text{O} = (13 \pm 3)\%$$

as the only possible value of the ratio which is reasonably consistent with all observations, including vacuum ultraviolet as well as mass spectra.

Dust Contribution to the Volatile Fraction

The large organic fraction of 33% (in mass) of the dust, found in the grains of comet Halley, brings new problems and new vistas related to the interface between dust and volatiles.

First, the organic fraction cannot be completely refractory, otherwise it would have survived the entry into the upper atmosphere and would therefore still be present in the pores of the Brownlee particles. The interpretation of recent data yields a total carbon content of 25% by weight, versus 5% in particles. The missing 20% carbon by weight cannot be too volatile either, otherwise it would have vaporized into the coma before being detected by the Giotto's neutral mass spectrometer. Table 10-3 suggests that it is combined with about 10% by weight of H, O, N, and that the fraction represents a total of 30% of the dust; in particular, 5.2% (by weight) of the dust seems to come from a couple of major constituents: formic acid and formaldehyde.

Table 10-3: Elemental Abundances in Comet Halley

Name of element	Dust (mass)	Gas (mass)	Total (mass %)
H	7.8	21.9	5.3%
C	72.0	29.1	18.1%
N	2.8	16.9	3.6%
O	104.0	194.1	53.4%
S	16.0	3.8	3.5%
Mg	17.0	—	3.0%
Si	28.0	—	5.0%
Fe	39.1	—	7.0%
A + Na	1.7	—	0.3%
Ca, Cr, Mn, Ni	4.0	—	0.7%
Totals	292.4	265.8	99.9%

All data were normalized to Silicon mass = 28, with dust to gas ratio = 1.1 (see text).

Assuming a primitive dust-to-ice mass ratio of 1.10 (see the Dust-to-Ice Ratio section), we have an amount of $\text{CO}/\text{H}_2\text{O} = 0.07$ that will be released in an extended source by a two-step process:

1. Vaporization of the CHON grains or CHON mantles, compatible with a characteristic lifetime of about 2×10^4 seconds;
2. Photodissociation of formic acid and formaldehyde into CO plus other molecular fragments, with a shorter lifetime, about 5×10^3 seconds for H_2CO and 2×10^3 seconds for HCO-OH , from their cross sections and the solar flux.

The CO flux produced by the extended source, as observed by mass spectrometry of the neutral gas, is $(13 \pm 4)\% \times 0.6 = (8 \pm 2)\%$ of H_2 , in reasonable agreement with the 7% deduced from the vaporization of the CHON grains.

We conclude that the release and photodissociation of formic acid and formaldehyde, which represent more than 5% by mass of the dust, can explain the total amount of CO released in an extended source of 15,000 km around the nucleus, as observed by the neutral mass spectrometer of Giotto.

We can generalize the previous approach and predict that the CHON grains are the source of other volatile species. A major one is hydrogen cyanide (HCN). HCN was already deduced to be the parent molecule of CN by quantitative arguments. Since it is present in the CHON grains, its slow release explains the persistence of the spiral-shaped CN jets observed in the coma of comet Halley. It can also be expected that CHON-type grains may play an important role in the exchange of matter between volatile dust and gas. During perihelion passage, their thermal evolution in the cometary mantle from volatile compounds (like formaldehyde) into stable dust (polyformaldehyde) could explain:

1. A slow evolution toward less gas and more dust (a larger and larger dust-to-ice mass ratio);
2. A slow transfer of carbon from gas to dust;
3. The disappearance of an excess source of carbon in the coma of evolved comets;
4. A reduction of the C/O ratio in the coma of evolved comets, depending on their perihelion distance and the number of their previous passages;
5. The claimed "puzzle" of the carbon abundance variation in the coma.

Elemental Balance Sheet of Comet Halley

To establish the elemental balance sheet of comet Halley, the gas phase and the solid phase must be combined in the proper ratios. The elemental ratios of the gas phase, given in table 10-1, result from a detailed discussion of the numerous data published from 1986 to 1988, which is needed to resolve the numerous inconsistencies found in the literature. The error bars of table 10-1 imply a value judgment about these inconsistencies. The whole discussion will not be repeated here (see Delsemme 1991 in Additional Reading for further details).

The elemental ratios for cometary dust are those given from the sum of 80 dust particles that hit the mass spectrometer on board the Vega 1 Spacecraft.

Table 10-4: Comparison of Elemental Abundances in Atom Numbers

Element	Solar	Comet Halley	Chondrites*		
			CI	CM	CV, CO
H	26600.0	30.0	2.0	1.0	0.10
C	11.7	8.0	0.7	0.4	0.08
N	2.3	1.4	0.05	0.04	0.01
O	18.4	18.8	7.5	5.3	4.10
S	0.5	0.6	0.5	0.2	0.12
Si	1.0	1.0	1.0	1.0	1.00

*Rounded averages.

Table 10-2 combines gas and dust by normalizing the amount of gas by the dust-to-gas mass ratio of 1.10. This ratio is confirmed by the fact that the dust composition is quasi-chondritic, but contains 3/4 of the total carbon of the comet, itself representing (when normalization to 1.10 is used) a nominal 3/4 of the cosmic carbon abundance.

Table 10-4 compares the elemental abundances in comet Halley from table 10-2 (expressed this time in atom numbers) with the solar and chondritic abundances. It is now quite clear that, except for hydrogen, depleted by a factor of almost 500, all the abundances of the light elements in comet Halley are within the error bars of solar abundances. The slight carbon deficiency may come from the variable CO^+ fraction blown away by the solar wind, hence not counted in its entirety in the atomic carbon line of the International Ultraviolet Explorer. The big carbon deficiency reported for other comets has disappeared entirely, mainly because of the large amount of carbon now detected in the dust. In the same way, the slight nitrogen deficiency may come from the N_2^+ depletion by dissociative recombination with electrons due to the magnetic confinement of the plasma in the onset of the tail. Undetected nitrogen could be blown away at high velocity in the plasma tail by this mechanism.

Quantitative Molecular Analysis of the Volatile Fraction

A useful tool to find discrepancies in the amount of the different molecular species detected by distinct methods (UV, visual, IR, or mass spectroscopy) is to build the balance sheet for all the elements of the molecules that have been observed or deduced, and verify that their sums reproduce (within the error bars) the elemental ratios observed or deduced in table 10-3.

The author has published a heuristic model of the chemical composition of Halley's volatile fraction, based on this technique. The model is reproduced in table 10-5. Each line of table 10-5 represents the contribution of each molecule to the elemental abundances. The total of each column gives therefore a number proportional to the total abundance of a particular element. The ratios of the totals must be compared with the elemental abundance ratios independently established and given in table 10-3.

The building of such a balance sheet for the elements remains difficult because of the large number of simultaneous constraints which are sometimes self contradictory. For instance, the known production rates for water and for oxygen-bearing compounds are in contradiction with the Pioneer Venus data that give $\text{H/O} = 1.4$. It is impossible to achieve an H/O ratio smaller than 1.8 (the ratio adopted in table 10-2) and it remains a feat to come close to it in table 10-4, because most other molecules add at least two hydrogen atoms per extra oxygen atom.

The only three molecules that are the exception are CO , CO_2 , and H_2CO_2 . However, the ratio $\text{CO}_2/\text{H}_2\text{O}$ has been measured and cannot be changed beyond its error bars. H_2CO_2 (formic acid) and H_2CO (formaldehyde), discovered in the organic fraction of the dust grains, are volatile enough to be counted in the volatile fraction: formaldehyde is much more volatile than water, and formic acid has almost exactly the same vapor pressure as water (it

Table 10-5: Chemical Composition of the Volatile Fraction of Comet Halley

Parent	%	H	C	O	N	S
H ₂ O	80	160	—	80	—	—
H ₂ CO ₂	4.5	9	4.5	9	—	—
H ₂ CO	4.0	8	4	4	—	—
CO ₂	3.5	—	3.5	7	—	—
CO	1.5	—	1.5	1.5	—	—
CH ₄	1.0	4	1	—	—	—
C ₂ H ₂	1.5	3	3	—	—	—
C ₃ H ₂	0.2	0.4	0.6	—	—	—
N ₂ H ₄	0.2	0.8	—	—	0.4	—
HCN	1.0	1.0	1	—	1	—
N ₂	0.5	—	—	—	1	—
H ₄ C ₅ N ₄	0.5	2	2.5	—	2	—
NH ₃	1.0	3	—	—	1	—
S ₂	0.2	—	—	—	—	0.4
H ₂ S	0.2	0.4	—	—	—	0.2
CS ₂	0.2	—	0.2	—	—	0.4
Totals:	100	191.6	21.8	101.5	5.4	1.0
	Ratios:	H/O	C/O	N/O	S/O	
	from table 10-2:	1.8 ± 0.4	0.20 ± 0.05	0.10 ± 0.05	0.01 ± 0.05	
	from this table:	1.89	0.21	0.05	0.01	

boils at 101°C). Both have been assumed to be the parent molecules for the extended source of CO that has been observed, since both photodissociate in times shorter than the vaporization of grain clusters. However, a fraction of this formaldehyde may be in polyformaldehyde; it has not been counted separately in table 10-4. An amount of formic acid somewhat larger than 4.5% would be beneficial to the balance of table 10-4, because it would improve the D/H ratio.

The total production of CO has been set at 10% of the volatiles, that is, 12.5% of the production of water; CO₂ is set at 3.5% of the volatiles (or 4.2% of water). The total production rate of CO and CO₂ has been pushed to the maximum compatible with the error bars of the observations to keep both H/O and C/O within reasonable limits.

Methane (CH₄) and ammonia (NH₃) represent altogether about 3 to 4% of water. Acetylene C₂H₂ is assumed to be the source of C₂ and C₃H₂ the source of C₃; C₃H₂ has now been shown to be abundant in interstellar space. Hydrogen cyanide is the source of CN. Finally, the "normal" ratios C₂: C₃: CN = 1.5 : 0.2 : 1 have been adopted here.

The amount of sulfur molecules is small enough not to interfere very much with the H and the C balance sheet. A more serious problem might turn out in the nitrogen balance. Hydrazine (N_2H_4) is the probable source of NH_2 , whereas NH_3 does not seem to be very abundant: a bonus for the balance sheet because NH_3 would introduce much hydrogen and no oxygen. It is also difficult to introduce more than 1% of N_2 as suggested by the small production rate of N_2^+ . A recent result reduces N_2 to a welcome 0.5%.

It is interesting to note that neither N_2 nor CO can be very abundant in a nucleus whose temperature is driven by the vaporization of water ice; this is because of the very large vapor pressure of N_2 and of CO. Even their clathrates have high dissociation pressures. Incidentally, the assumption that carbon monoxide can form a clathrate with water has been recently confirmed. It has a dissociation pressure of 1256 bars at 273 K and it lies, therefore, between the oxygen and the nitrogen clathrates in stability.

The observed presence of purine ($\text{H}_4\text{C}_5\text{N}_4$) in the organic fraction of the dust, must not be taken at its face value in table 10-5. It has been used here as a symbol and a reminder that we may still have several unknown organic compounds in the dust that might dissociate or vaporize into the coma.

Altogether, our understanding of the volatile fraction has considerably improved with comet Halley. The major recent achievement is, of course, the understanding that a very large fraction of the dust is volatile enough to be the origin of an extended source of gas in the inner coma. However, most of the exobiology questions remain pending. In particular, those about purines and pyrimidines must wait for a rendezvous mission to a comet.

Isotopic Ratios

Before comet Halley, the only isotopic ratio approximately measured in comets was $^{12}\text{C}/^{13}\text{C}$, but the error bars were so large that it was impossible to say whether it was really different from 89, the terrestrial ratio.

With the flybys of comet Halley, new isotopic ratios have been measured. It has been reported that the Giotto neutral mass spectrometer gives a D/H ratio between 60 and 480 ppm, implying that the cometary deuterium is enriched by a factor of at least 3 with respect to interstellar hydrogen, or to hydrogen in Jupiter and Saturn. A comparable enrichment occurs in terrestrial water, suggesting that water on the terrestrial planets can be of cometary origin, an idea that was proposed earlier by models of the accretion of the planets from the solar nebula, and that is described in detail in the second part of this chapter.

It also has been reported that $^{18}\text{O}/^{16}\text{O} = (23 \pm 6)10^{-4}$ in comet Halley, agreeing within the error limits, with the average solar system value of 20×10^{-4} . Although we still lack much data, nothing has been found yet that would be inconsistent with cometary material originating from the same reservoir as the rest of the solar system.

Exogenous Origin of Carbon on Terrestrial Planets

Another interface between comets and exobiology cannot be neglected here; it concerns the exogenous origin of carbon on the terrestrial planets and, in particular, the origin of what became the biosphere on Earth.

The origin of carbon on the terrestrial planets is not trivial because there is mounting evidence that, at a time when the largest planetary bodies were micrometer-sized grains of dust, there was a high-temperature period in the zones of the future terrestrial planets; hence all dust was outgassed and most carbon was stored as CO in the gas phase just before planetesimals formed.

Evidence for a High-Temperature Phase

The formation of single stars generally implies the transient existence of an accretion disk. Such a disk is needed to get rid of the excess angular momentum during the collapse of an interstellar cloud nodule. The disk stops the free-fall collapse of the cloud; viscous friction brakes its fast-turning inner layers and accelerates the more slowly turning outer layers. As a result, mass is transported inward and feeds the central star, whereas the excess angular momentum is transported outward and widens the disk.

The theoretical analysis has been recently supported by the discovery of many dust disks surrounding young stars. First, the Infrared Astronomical Satellite (IRAS) detected large infrared excesses near 100 micrometers in the spectra of many young stars. Their interpretation as dust disks was confirmed in particular by a photograph of the dust disk of Beta Pictoris.

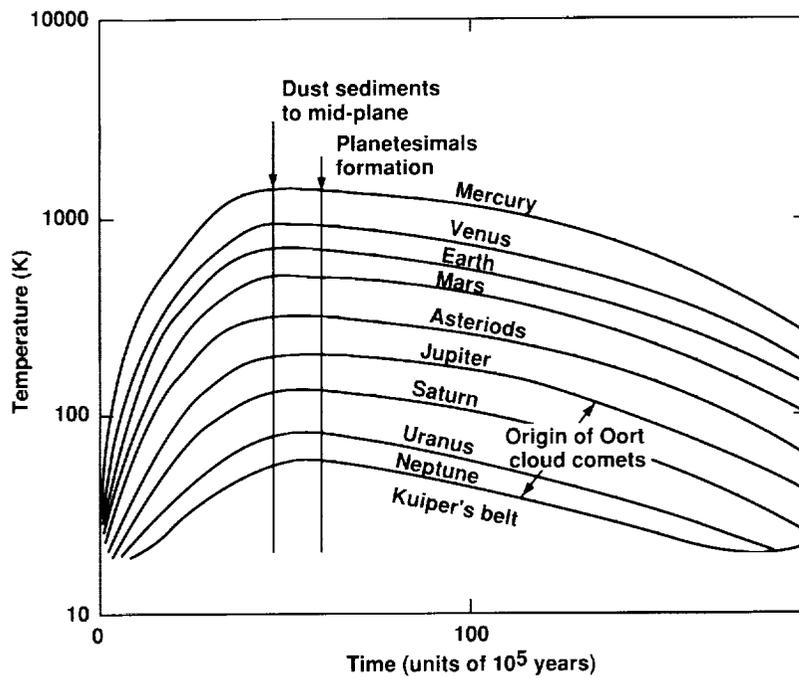


Figure 10-1. Typical example of the variation of the gas temperature in the accretion disk in the various regions of planetary formation.

A common feature of the different models of viscous accretion disks is that the temperature dependence on heliocentric distance r follows a law close to $r^{-3/4}$, regardless of the details of the viscous mechanism. However, this temperature varies with time (see fig. 10-1): it grows steadily during the collapse of the interstellar cloud that feeds the disk and starts falling as soon as the accretion subsides and stops. Typically, the temperature varies with $(\dot{M}M)^{1/4}$,

M being the total mass (disk plus star) and \dot{M} the mass accretion rate. For reasonable values of the parameters, for instance $M = 1M_{\odot}$ and $\dot{M} = 10^{-5} M_{\odot} \text{ yr}^{-1}$, the maximum temperature reached at each heliocentric distance is reasonably consistent with those inferred from the chemical constitution of the terrestrial planets. The temperature gradient inferred is also consistent with the $r^{-3/4}$ law deduced for simple viscous disks. More sophisticated models give a slightly different temperature gradient for the mid-plane temperature

(for instance in $r^{-9/10}$), giving an even better agreement.

In this model, the existence of reduced iron in the nucleus of the Earth is explained by the reduction of iron in the fine dust grains of the disk which are in contact with a large amount of H_2 at a temperature close to 900 K. Iron must be reduced before the accretion of dust into large objects; there is no way to reduce iron after it has reached the Earth's mantle in the form of an oxide or silicate.

Using such a high temperature for the Earth's zone of accretion, the $r^{-3/4}$ dependence on distance predicts 450 K near 2.6 AU, which is the place beyond which the C asteroids start to outnumber the S asteroids. There is a strong suggestion (from infrared spectra and very low albedos) that carbonaceous chondrites come from the C asteroids, and 450 K is the temperature required to separate the formation of ordinary from carbonaceous chondrites. These two examples are sufficient to illustrate the type of indirect arguments that can be used to support this fossil evidence, but there are several others that result in the same conclusions.

Now let's consider models of the accretion disk when it reaches its maximum temperature. Figure 10-2 illustrates three adiabats for the gas in the mid-plane of the accretion disk at that moment. These adiabats have been traced for illustrative purposes only. The symbols for the planets are located in the center of their accretion zones. To satisfy the previous temperature requirements, model C has too much mass and model D not enough. Model CD has been selected by interpolating models C and D; it fits in with the previously derived formation temperature of the planets. The three adiabats have been superimposed on a thermochemical diagram giving the different domains of the major molecular species for a gas of solar composition. The three adiabats show that, in the zones of the terrestrial planets, carbon is in the form of gaseous CO. The three adiabats have the advantage of showing the extreme range that would remain consistent with planetary data, like for model D the reduction of the Earth's core, or for model C the existence of carbonaceous chondrites at 2.6 AU in the asteroid belt.

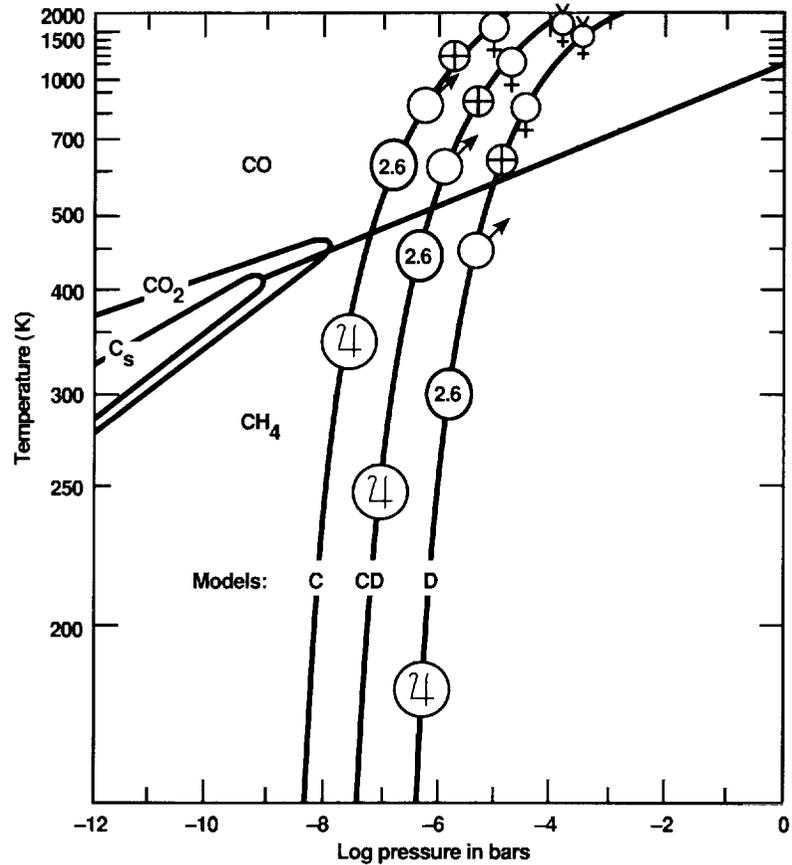


Figure 10-2. The thermochemical equilibrium diagram of the carbon compounds in a gas of solar composition. The three quasi-vertical curves represent three adiabats through the mid-plane of the accretion disk at the time of its maximum temperature. Models C and D correspond to solar-nebula models C and D; model CD is a linear interpolation of the two previous models that fits in better with an empirical adiabat derived from the planets' chemical composition. The other solid lines separate the domains in which CH_4 , CO, CO_2 , and graphite (C_s) are the most abundant carbon compounds. The activity of graphite is a maximum not far from the line separating CO and CH_4 . All adiabats compatible with planetary chemistry show that the terrestrial planets' formation took place in a hot portion of the accretion disk, where a large hydrogen excess reduced and dehydrated all dust grains. The symbols of the planets locate their zones of formation. The figure 2.6 in a circle refers to 2.6 AU, beyond which the C asteroids begin to outnumber the S asteroids. The infrared spectra and dark albedo of the C asteroids suggest carbonaceous chondritic material, hence the activity of graphite should be near maximum a bit beyond 2.6 AU. This implies that the grains of the Earth's zone were too hot to contain enough carbon or water. The bulk of our oceans and of our carbonates must therefore have an exogenous origin.

To establish whether thermochemical equilibrium is reached, we must compare the durations available in the accretion disk with the time constants of the chemical kinetics. The durations in the disk are given by the models. In particular, the trend toward equilibrium will begin only when large-scale turbulence subsides and stops. At that time, several quasi simultaneous events occur quickly (see fig. 10-1): the maximum temperature is reached; the Sun's mass stops growing; and the dust sediments and forms thin dusty rings in the mid-plane, where it starts accreting into larger solid objects (the planetesimals). This is a very effective way to separate solids from gas before the temperature drops. A duration of 10^3 to 10^4 years is available to reach thermochemical equilibrium in the disk. The end of that duration occurs as soon as solids are effectively removed from the gas, that is, when dust has agglomerated into boulders of at least a few meters in diameter.

Lewis and co-workers have examined the chemical kinetics of a gas of solar composition. The largest chemical time constants that are significant turn out to be of the order of one century near 1000 K; therefore thermochemical equilibrium will be reached before solids are separated from the gas phase. It is concluded that the dust has been completely outgassed, dehydrated, and reduced in the zone of the terrestrial planets, before its incorporation into planetesimals, and eventually into planetary bodies.

These researchers have also carefully considered the carbon problem, and they have been puzzled by the retention of carbon in the terrestrial planets. Searching for a mechanism of carbon retention for the terrestrial planets, Lewis and co-workers have deduced that the only way to imprison carbon in the solid phase is to put it in solution in metallic iron grains, but its amount would still be two or three times smaller than the observed amount of carbon on Earth and Venus.

Their choice for the adiabat has, however, put the Earth's zone near the peak of graphite activity; for any adiabat, graphite activity goes through a maximum in the vicinity of the line separating, on figure 10-2, the domains of CH_4 and CO. Adiabat CD in figure 10-2 puts the formation temperature of the carbonaceous chondrites (assumed to form at 2.6 AU and beyond) from 300 to 450 K in agreement with other assessments, and close to the maximum of graphite activity, favorable for Fischer-Tropsch type reactions. But this removes the Earth's zone of accretion from the maximum of graphite activity; the amount of carbon available for the Earth and Venus becomes several hundred times smaller than the observed amount on these planets. Hence the interpretation of the organic compounds in carbonaceous chondrites as the result of Fischer-Tropsch-type reactions strongly implies that the bulk of the observed carbon compounds on the terrestrial planets has an exogenic origin.

From Planetesimals to Planets

After accretion of planetesimals, the pace slows down drastically. Larger planetary embryos grow from numerous collisions. It has been established that collisional velocities grow in proportion to the size of the largest objects. The reason is that the growing gravitation of the embryos deflects the smaller bodies into more elliptical orbits. This means that the zone feeding a protoplanet becomes wider and wider; objects deflected by the giant protoplanets may come closer and may eventually hit the Earth. Since these objects come from colder zones (see fig. 10-1) they contain snow and organic matter; hence the final steps of accretion become heterogeneous.

A Veneer of Volatile and Organic Material

Siliceous planetesimals originating in the zones of the terrestrial planets were probably considerably depleted when these planets reached 90% of their masses. Since the accretion of the giant planets took longer (at least for Uranus and Neptune) the diffusion of the planetesimals coming from larger and larger distances took longer and longer, implying that the ordinary chondrites arrived first (say from 1.6 to 3.6 AU, possibly bringing 7% of the final mass); the carbonaceous chondrites arrived later (possibly 2% of the final mass, from 2.6 to 5 AU); the comets arrived last, bringing 1% of the final mass from 5 to 50 AU and beyond. Oxidized material being added as a late veneer achieved the high oxidation state of the Earth's crust.

Cometary Contribution

Using a model from 1972, the author assessed that the total mass of comets hitting the Earth at the end of accretion was large enough to explain all the water in the oceans and all the carbonates and organic matter on the Earth (from table 10-5, in round figures, water represents 40% of the cometary mass and organic matter more than 20%).

Better evaluations have now been made. Others have found that comets have brought four times as much water as the mass of our oceans. Still other researchers have found ten times the present mass of water. It has also been determined that the total mass of water in the oceans is explained if only 10% of the extant lunar craters are due to comets. The present amount of water and carbon on the Earth is consistent with a considerable erosion of the atmosphere and oceans, due to the last giant impacts at the end of the accretion period. These giant impacts are predicted by the accretion theory, and their remnants are visible

everywhere (Hellas Planitia on Mars, Mare Imbrium on the Moon, Caloris basin on Mercury, etc.). Giant impacts probably explain the origin of the Moon, as well as the considerable erosion of the atmosphere on Mars because of its small gravity.

The amount of organic material brought down to Earth during the accretion period (up to some 3.8 billion years ago) was somewhat larger than half the mass of the oceans, although the most volatile part may have been considerably eroded by giant impacts. Only an extremely small fraction of such a mass needs to be preserved in the form of prebiotic compounds to completely overthrow the traditional picture in which the first prebiotic syntheses occurred on Earth.

Concluding Remarks

The transfer of organic compounds from interstellar space to the outskirts of a proto-planetary disk, their accretion into cometary objects, and the transport of the latter into the inner solar system by orbital diffusion throw a new light on the central problem of exobiology. It suggests the existence of a cosmic mechanism, working everywhere, that can supply prebiotic compounds to ubiquitous rocky planets, in search of the proper environment (proper redox ratio, liquid water, etc.) to start life in many places in the Universe.

However, we do not know enough about cometary chemistry to answer most of the exobiology questions. The multiple flybys close to the nucleus of comet Halley have brought a wealth of new information on comets, in general, and have come tantalizingly close to answering important exobiology questions. Nonetheless, the answers have been left in doubt mostly because the fast flyby velocity destroyed significant molecules.

We need other cometary missions if we want to answer these exobiology questions. The first prerequisite is a rendezvous mission, that is, a mission whose relative velocity to the cometary nucleus can be brought down to a few meters per second. In such a mission, we also need a penetrator to reach pristine material a few feet under the surface layer that has been modified by irradiation and vaporization. Later on, it is clear that only a sample return mission will be able to answer the final questions, but such a mission cannot be prepared in haste before having studied a cometary nucleus from nearby. A rendezvous mission is therefore a prerequisite for clarifying sampling techniques.

The choice of a proper comet is also an important consideration. Until recently, short-period comets were considered as a last resort because they are the only ones whose orbits are known sufficiently ahead of time to prepare a mission, but the "new" comets (coming straight from the Oort cloud, where they had been kept in the deep cold of space) were considered more "pristine" than short-period comets. Recently however, it has been established that the orbital diffusion of comets cannot produce the flattened symmetry of the system of short-period comets, if their source does

not already have the same flattened symmetry. It has been deduced that the source of the short-period comets is not the (quasi-spherical) Oort cloud, but the Kuiper belt proposed in 1951. The Kuiper belt would be a remnant of the accretion disk (like the one around Beta Pictoris) where cometesimals never formed planets. Figure 10-1 shows that the maximum temperature in the Kuiper belt never exceeded 40 K, whereas other mechanisms put the source of the Oort cloud comets in the zones of the giant planets (the diffusion of their orbits is due to the growing embryos of the giant planets), where the temperature reached from 50 to 180 K. Paradoxically, the short-period comets, at least before entering the inner solar system, could be more pristine objects than the Oort cloud comets (this giant reservoir from which all long-period comets originate). Short-period comets that have entered the inner solar system only very recently and which have perihelion distances as large as possible represent the best targets of opportunity for exobiology studies.

Additional Reading

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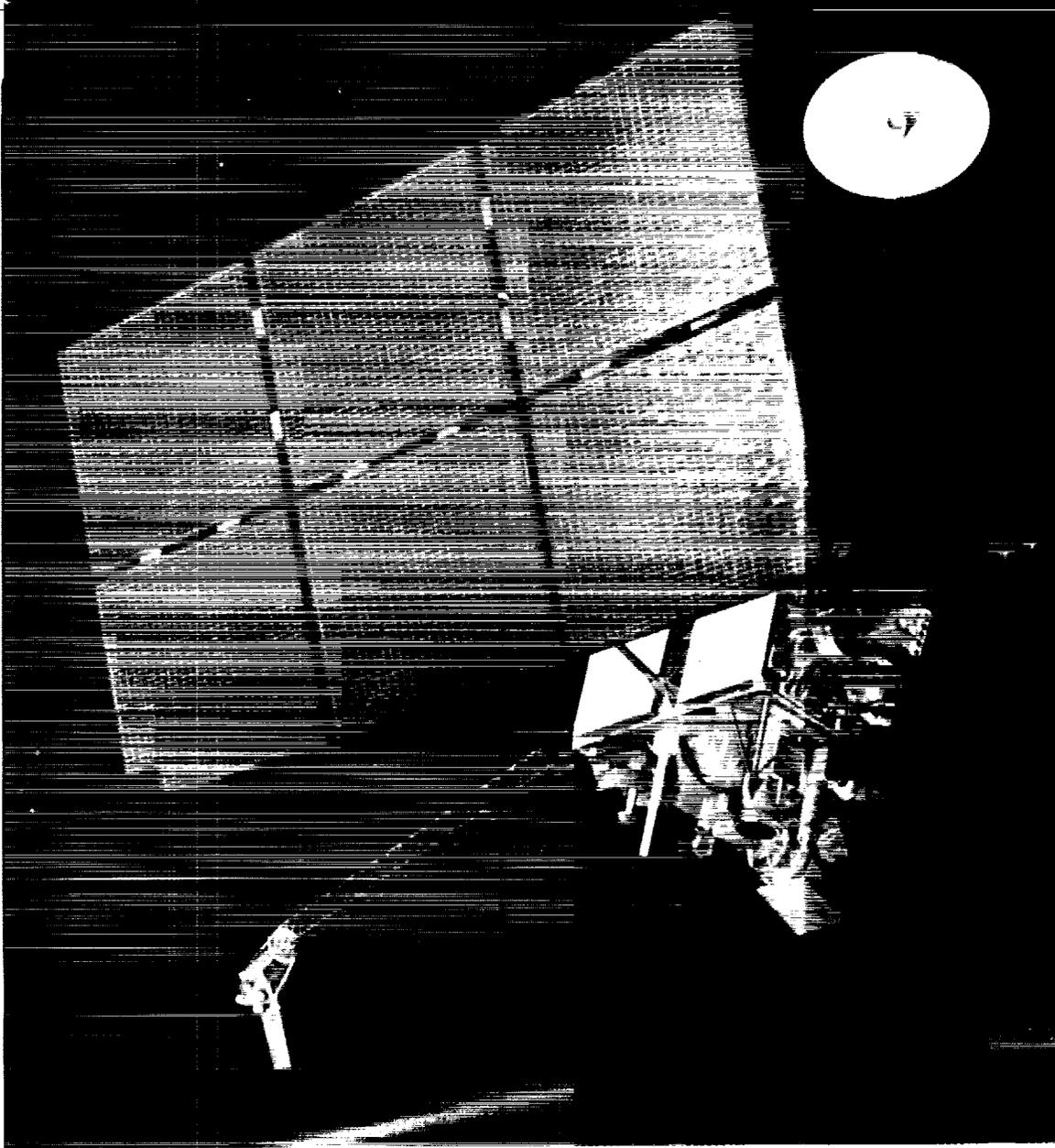
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